Effects of Poly(acrylic acid) Electrosteric Stabilizer on Entry and Exit in Emulsion Polymerization

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Received January 16, 1996; Revised Manuscript Received April 29, 1996[⊗]

ABSTRACT: A methodology developed to obtain rate coefficients for entry and exit (desorption) in emulsion polymerizations was applied to systems stabilized electrosterically by a copolymer of acrylic acid and styrene embedded in a styrene seed particle. This was grown as a second-stage procedure, by adding styrene and acrylic acid to a styrene seed and then polymerizing. Rate coefficients for entry (ρ) and exit (k) for subsequent homopolymerization of the resulting latices with styrene were obtained from the time dependence of the approach to steady state using both chemical and γ-radiolytic initiation; the latter was used in relaxation mode, which measures k directly. Compared to the same latices with an electrostatic stabilizer, at pH 7 the electrosteric stabilizer greatly reduced both ρ and k. When ionic strength was increased, ρ increased relative to that found for electrosterically stabilized latex in the absence of added electrolyte. For electrostatically-stabilized latices, entry is supposed to occur by aqueous-phase propagation to a critical degree of polymerization z which then undergoes irreversible entry; the present data for electrostatically-stabilized latices support this model, including its prediction that ρ be independent of particle size, all other things being equal. The decrease in ρ in the electrosterically-stabilized latices is ascribed to a "hairy" layer through which diffusion of a z-mer is slow, so that it may be terminated prior to actual entry. For electrostatically-stabilized latices, exit is supposed to occur by transfer, resulting in a monomeric radical which exits by diffusing through the aqueous phase, this event competing with intraparticle propagation; the decrease in k in the electrosterically-stabilized latices (also seen in other polymerically-stabilized systems) can be interpreted by assuming that aqueous-phase diffusion is slower in the hairy layer.

1. Introduction

Industrial emulsion polymerization formulations frequently involve water-soluble comonomers such as acrylic, methacrylic, and itaconic acids; latices so prepared are very robust in their colloidal stability.[1,2] In view of the widespread industrial usage of various forms of polymeric surfactant in emulsion polymerizations, there is a need for improved knowledge of the mechanisms of events involving the interface in such systems: specifically, the phase-transfer events of radical entry and exit (desorption). Extensive mechanistic studies have led to models for entry into, and exit from, latex particles in emulsion polymerization which are stabilized by ionic surfactants (e.g., refs 3 and 4). The objective of this paper is to carry out such studies for an architypal electrosterically-stabilized system which is similar to, but simpler than, that typical of many industrial formulations.

The postulated mechanisms for entry and exit, which were deduced from extensive data chosen to be sensitive to entry and exit events, are, in brief, as follows.

(a) Entry starts with aqueous-phase propagation to a critical degree of polymerization z which then undergoes irreversible entry (no smaller degree of polymerization being able to enter), the aqueous-phase propagation of radicals with degree of polymerization less than z also competing with aqueous-phase termination.[5] The actual entry of a z-mer is supposed to be so fast as not to be rate-determining; the rate-determining steps for entry are instead initiator dissociation and aqueous-phase propagation and termination.

(b) Exit occurs by transfer to a monomeric radical inside the particle; this monomeric radical escapes by diffusing through the aqueous phase, this event competing with intraparticle propagation.[6−8]

While there is good evidence for these mechanisms in the emulsion polymerizations of a number of monomers[4,9−14] (including copolymerizations[15]), all these studies have used ionically-stabilized latexes. However, there are hints that these models may break down with latexes which are stabilized by polymeric surfactant. For example,[16] the exit rate coefficient in a styrene latex stabilized with poly(ethylene oxide)−nonylphenol (with a mean degree of polymerization of 30) gave an exit rate coefficient an order of magnitude smaller than that for latex particles in ionically-stabilized particles of the same size. This suggests an impediment of some sort to desorption of a monomeric radical, and such an impediment could well have some effect on the entry from the aqueous phase of a z-meric initiator-derived radical.

In the present studies, well-established methods for measuring entry and exit rate coefficients[3] are applied to polymerically (or more specifically, *electrosterically*[2,17]) stabilized latices which are models for a type commonly used in industry: a block copolymer of acrylic acid and styrene. These are formed by coating a styrene seed with a small amount of stabilizer, as a second-stage procedure, by adding styrene and 3% (w/w) acrylic acid to the latex and polymerizing to about 5% conversion; no secondary particle formation took place. The change in size on the second-stage growth required to form the electrosteric stabilizer is relatively small (5 nm was the largest value). The reason this second-stage procedure is adopted is that the methods for obtaining the entry and exit rate coefficients require seeded growth. By comparing the rate coefficients obtained for these latexes with both electrosteric and ionic stabilizer, it is possible to compare directly any effects of electrosteric stabilizer compared to the well-understood mechanisms for ionically-stabilized latices. Because the poly(acrylic acid) (pAA) moiety of the electrosteric stabilizer would be sensitive to both pH and ionic strength, the variation

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

S0024-9297(96)00056-3 CCC: $12.00 © 1996 American Chemical Society

of the entry and exit rate coefficients with both these quantities will be examined.

The above procedure for growing the electrosteric stabilizer was chosen because it is similar to the way water-soluble comonomers such as acrylic acid are used in commercial latex preparations. Admittedly, the electrosteric stabilizers so formed are not well characterized (in comparison to careful studies using well-characterized block copolymer with large acrylic acid segments[1]). However, it is likely that they comprise relatively long chains of pAA formed by aqueous-phase propagation, which then enter the latex particle after propagating with one or more styrene units in the aqueous phase; subsequent propagation in the styrene-rich interior of the particle would result in a well-anchored pAA (or polyacrylate, depending on the pH) chain extending into the aqueous phase. No attempt is made in the present paper to characterize the lengths of the pAA chain; instead, our objective is to see whether or not the presence of such stabilizer exerts a significant effect on entry and/or exit. If such an effect is seen, then future studies can be directed toward systems which are more easily characterized (see, e.g., ref 1).

There was no appreciable decrease in the colloidal stability of the electrosterically-stabilized latex at pH 4, compared to that at pH 7. However, the electrostatically-stabilized latex shows an appreciable decrease in colloidal stability at pH 4, compared to that at pH 7.

At pH 4, the dissociation rate coefficient for $K_2S_2O_8$ is the same as that at pH 7.[18]

The overall method for obtaining entry and exit rate coefficients is as follows.[3]

(1) All studies are performed on seeded systems, care being taken to avoid secondary particle formation (this is because the method explicitly requires a fixed, known particle number, N_c).

(2) Both the steady-state polymerization rate and the approach to steady state are measured; data on the approach to steady state can only be used if they are free of inhibitor and equilibration artifacts (the latter can occur if the time required for all materials in the dilatometer to reach thermal equilibrium after they have been mixed in the reaction vessel exceeds the induction period).

(3) Initiator is both with a chemical initiator (persulfate in the present instance) and with γ radiolysis; the latter is used in the relaxation mode, i.e., the polymerization vessel is removed from the radiation source, and the relaxation behavior (rate of approach to a new steady state in the absence of external initiator) is monitored.

(4) To study entry and exit, conditions are chosen so that the system obeys "zero–one" kinetics, i.e., such that entry of a radical into a particle already containing a growing radical results in "instantaneous" termination, so that all particles contain only zero or one growing radical (this is a combination of Smith–Ewart cases 1 and 2).

(5) Rate data in zero–one systems are sensitive only to entry and exit, and, in particular, γ radiolysis relaxation data are dominated by exit, which is usually a rate-determining step for radical loss. Given an exit rate coefficient from γ relaxation, the entry rate coefficient in a chemically-initiated system can then be obtained solely from its steady-state rate, even if the *approach* to this steady state is contaminated with inhibitor and/or equilibration artifacts.

(6) The rate coefficients for entry and exit can be obtained from the type of data so described, given an assumed fate of exited radicals (i.e., whether they (a) terminate completely in the aqueous phase, (b) always reenter another particle and remain there, or (c) always reenter another particle but reescape unless that particle contains a growing radical, in which case instantaneous termination ensues). Even if the fate of exited radicals is uncertain, this would at worst result in an uncertainty of about 50% in the rate coefficients for entry and exit, and it will be seen that the effect of electrosteric stabilizer in these systems, compared to that in ionically-stabilized ones, is much greater than this uncertainty.

(7) A styrene system was chosen for study here, because there have been extensive studies of the entry and exit events for this monomer,[11,16,19–26] including evidence that the fate of exited radicals is to undergo reentry and remain within the new particle.

2. Summary of Background Theory

In a seeded emulsion polymerization, the polymerization rate R_p is given by:

$$R_p = k_p \frac{N_c}{N_A} \bar{n} C_p \tag{1}$$

where k_p is the propagation rate coefficient, N_c the number of particles per unit volume of aqueous phase, N_A Avogadro's constant, and C_p the monomer concentration in the latex particles. For styrene at 50 °C, the value of k_p has been obtained with good accuracy;[27] $k_p = 2.6 \times 10^2$ dm^3 mol^{-1} s^{-1} was taken as the value for the present studies. For styrene latices such as those used here, the saturated value of C_p is 5.5 mol dm^{-3} at 50 °C.[19] If (as has been shown[11] to be the case for styrene systems such as those used here) all exited radicals reenter another particle and remain there ("Limit 2a"[3]), the time evolution of the average number of radicals per particle, $\bar{n}$, is given by:

$$d\bar{n}/dt = \rho(1 - 2\bar{n}) - 2k\bar{n}^2 \tag{2}$$

where ρ is the total entry rate coefficient ($\rho = \rho_{\text{initiator}}$ and ρ_{thermal}, the last quantities being respectively the components of the entry rate coefficient arising from chemical or radiolytic initiator and from "background thermal" initiation), and k is the phenomenological exit rate coefficient. Fitting of the solution of eq 2 to conversion/time data yields ρ and k, if one has both the steady-state rate and the rate of approach to this steady state (the actual means of data fitting is the "slope-and-intercept" method[3,19,28]). Relaxation data can always be so treated, since the second and subsequent removal from the source will always be free of inhibitor and equilibration artifacts. Such artifacts will not always be absent from chemically-initiated runs; however, in such cases the value of ρ was obtained from the steady-state form of eq 2:

$$\rho = \frac{2k\bar{n}^2}{1 - 2\bar{n}} \tag{3}$$

using the steady-state value of $\bar{n}$ for chemical initiation and a value of k for the same latex from a relaxation run.

Using the models for exit described above and assuming that there is no barrier to transport of a monomeric radical between the particle and water phases, the value of k is given by:[29−32]

$$k = \frac{3D_{\mathrm{W}}}{r_{\mathrm{s}}^{2}} \frac{k_{\mathrm{tr}}}{k_{\mathrm{p}}^{1}} \frac{C_{\mathrm{W}}}{C_{\mathrm{P}}} \tag{4}$$

where D_{W} is the diffusion coefficient of the radical in water, k_{tr} and k_{p}^{1} the rate coefficients for transfer to monomer (or to whatever species exits) and for intraparticle propagation of this species, C_{W} the concentration of monomer in the aqueous phase, and r_{s} the swollen particle radius.

The mechanism for entry described above involves the following steps:

$$\mathrm{I_2}^{-} \xrightarrow{k_{\mathrm{d}}} 2\mathrm{I}^{\bullet -} \tag{5}$$

$$\mathrm{I}^{\bullet -} + \mathrm{M_{aq}} \rightarrow {}^{-}\mathrm{IM}^{\bullet} \quad \text{(fast, not rate-determining)} \tag{6}$$

$${}^{-}\mathrm{IM}_{i}^{\bullet} + \mathrm{M_{aq}} \xrightarrow{k_{\mathrm{p,aq}}^{i}} {}^{-}\mathrm{IM}_{i+1}^{\bullet}, \qquad i < z \tag{7}$$

$${}^{-}\mathrm{IM}_{z}^{\bullet} + \text{particle} \rightarrow \text{entry} \quad \text{(fast, not rate-determining)} \tag{8}$$

where $\mathrm{M_{aq}}$ is a monomer unit in the aqueous phase. Solution of the corresponding rate equations leads to the following set of equations which are solved iteratively to yield $\rho_{\mathrm{initiator}}$:[5]

$$\rho_{\mathrm{initiator}} = \frac{N_{\mathrm{A}}}{N_{\mathrm{c}}} k_{\mathrm{p,aq}}^{z-1} C_{\mathrm{W}} [{}^{-}\mathrm{IM}_{z-1}^{\bullet}];$$

$$[\mathrm{IM}_{i}] = \frac{k_{\mathrm{p,aq}}^{i-1} [{}^{-}\mathrm{IM}_{i-1}^{\bullet}] C_{\mathrm{W}}}{k_{\mathrm{p,aq}}^{i} C_{\mathrm{W}} + k_{\mathrm{t,aq}}[\mathrm{T}]}$$

$$[\mathrm{IM}_{1}] = \frac{2f' k_{\mathrm{d}}[\mathrm{I}]}{k_{\mathrm{p,aq}}^{1} C_{\mathrm{W}} + k_{\mathrm{t,aq}}[\mathrm{T}]}; \qquad [\mathrm{T}] = \sum_{i=1}^{z-1} [{}^{-}\mathrm{IM}_{i}^{\bullet}] \tag{9}$$

where [I] is the initiator concentration, k_{d} the initiator dissociation rate coefficient, and f' the efficiency for aqueous-phase dissociation (f' is typically 0.6 and is *not* the same as entry efficiency, which is much lower), $k_{\mathrm{t,aq}}$ the termination rate coefficient in the aqueous phase (which, for simplicity, is assumed independent of chain length), $k_{\mathrm{p,aq}}^{\mathrm{i}}$ the aqueous-phase propagation rate coefficient of an i-meric radical (IM_{i}) derived from initiator, and [T] the total radical concentration in the aqueous phase. If the $k_{\mathrm{p,aq}}^{\mathrm{i}}$ are assumed independent of chain length, then eqs 9 have an analytic solution:

$$\rho_{\mathrm{initiator}} \approx \frac{2f' k_{\mathrm{d}}[\mathrm{I}] N_{\mathrm{A}}}{N_{\mathrm{c}}} \left\{ \frac{\surd(2f' k_{\mathrm{d}}[\mathrm{I}] k_{\mathrm{t,aq}})^{1/2}}{k_{\mathrm{p,aq}} C_{\mathrm{W}}} + 1 \right\}^{1-z} \tag{10}$$

Note that this mechanism, and the corresponding quantitative relations of eqs 9, states that the value of $\rho_{\mathrm{initiator}}$ will be independent of particle size for two latices with the same particle number and initiator concentration and differing only in radius. This prediction will be tested as part of the present work.

3. Experimental Section

All runs were performed at 50 °C. Styrene was supplied by Aldrich Chemical Co. Prior to use the inhibitor, hydroquinone, was removed by washing the styrene in a 5% sodium hydroxide solution until no yellow color was observed in the aqueous phase. The styrene was then washed with distilled water, followed by 1% hydrochloric acid solution to remove residual hydroxide. The styrene was then dried overnight over anhydrous calcium chloride before distilling at reduced pressure (bp 50 °C) and stored under refrigeration for no more than 2 weeks prior to use.

Table 1. Recipes for Electrostatically- and Electrosterically-Stabilized Latices

component	mass (g)	
	ECST	EMST
styrene	25.03	584.4
AMA 80	14.36	25.58
$NaHCO_3$	1.12	2.22
H_2O	881.1	1395.5
$K_2S_2O_8$	2.71	2.24
$FeSO_4{\cdot}7H_2O$	0.027	
radius (nm)	24	44
standard deviation (nm)	5	3
polydispersity	1.1	1.1
solids (w/w %)	2.5	26.3

component	mass (g)	
	ECSTA	EMSTA
latex (as dry weight of polymer)	11.55 (of ECST)	63.10 (of EMST)
styrene	2.04	20.8
acrylic acid	0.599	1.11
$K_2S_2O_8$	0.0286	0.0218
added water	20	416
AMA 80	0.5	1.1
radius (nm)	25	49
standard deviation (nm)	4	3
polydispersity	1.1	1.1
solids (w/w %)	2	12.2

Acrylic acid (Aldrich Chemical Co.) was distilled under reduced pressure (bp 44 °C) and stored under refrigeration before use. Any inhibitor was not removed from acrylic acid by washing, as the amount of acrylic acid used in any polymerization was small and the residual inhibitor remaining after distillation would be small. The toxicity of the monomer also made it preferable that as few procedures as possible were performed.

Potassium persulfate (Ajax Chemicals, AR Grade) was used without further purification. Aerosol MA 80 (AMA 80, National Starch and Chemicals) was used without further purification.

Two seed latexes, ECST and EMST, were prepared following standard recipes and procedures,[11,33] given in Table 1. Monomer, surfactant, $NaHCO_3$, and water were emulsified in a bottle polymerizer for 1 h at 80 °C for ECST and 90 °C for EMST. Sufficient water to dissolve the initiator was retained and used in dissolving the initiator in a separate container. The bottle was then opened and the preheated initiator solution added. The bottle was resealed and replaced in the bottle polymerizer. The reaction mixture was then left to polymerize for approximately 18 h. The resulting latex was dialyzed for 1 week against distilled water, with the water being changed three times each day. This treatment would remove any residual monomer and most water-soluble oligomers. The latex was then filtered through glass wool to remove any coagulum.

Particle size and polydispersity were obtained by the use of capillary hydrodynamic fractionation, CHDF (see below).

The electrosterically-stabilized latexes were prepared by embedding polymer onto the surface of a portion of the existing latexes, EMST and ECST. The recipes used are included in Table 1. Poly(acrylic acid) was embedded into EMST, to form latex EMSTA, and into ECST, to form ECSTA, as follows. Styrene monomer was allowed to swell the latex for 45 min at 50 °C in the presence of AMA 80. Acrylic acid was then added, followed by the initiator solution about 20 s later, and allowed to react for 20 min, under a positive pressure of nitrogen. The

Table 2. Typical Recipes for Seeded Dilatometry Runs

	mass (g)	
component	24 nm latex	44 nm latex
seed latex	0.2	1
styrene	2.5	3
AMA 80	0.3	0.3
$K_2S_2O_8$	0.002	0.002
added water	60	60

reaction was terminated by exposure to oxygen and the resulting latex dialyzed for 1 week against distilled water with three water changes daily. The resulting latex was then filtered through glass wool to remove coagulum. Particle size and the absence of secondary nucleation were determined using CHDF. No secondary nucleation was observed. The result is assumed to be a block copolymer of acrylic acid and styrene, embedded into the latex particle, with the hydrophilic poly(acrylic acid) moiety located in the interfacial and aqueous phase regions.

Kinetics were monitored using automated dilatometry. Latex and distilled water were placed in the reaction vessel and degassed under reduced pressure for at least 10 min, with constant agitation. Surfactant, monomer, and any other additives to the system (e.g., to change pH or ionic strength) were added, and the system was allowed to equilibrate for a minimum of 8 h under ambient conditions. The mixture was then heated to the reaction temperature of 50 °C, to which was then added initiator, previously dissolved in degassed, distilled water and heated to 50 °C.

Typical recipes for chemically-initiated dilatometry are given in Table 2. The amounts of latex and monomer were chosen to give an Interval II reaction (i.e., monomer droplets still present) and the same N_c for both size particles. Initiator concentrations were chosen to be sufficiently low as to avoid secondary reactions but also high enough to give an entry rate coefficient significantly higher than the thermal[3] entry rate coefficient. Ionic surfactant (AMA 80) was added to maintain the monomer emulsion in both electrostatically- and polymerically-stabilized latex. In the case of electrostatically-stabilized latex, the ionic surfactant also stabilized the latex particles.

For γ-radiolysis initiation, the reaction mixtures were prepared by the same method as chemically-initiated runs, without chemical initiator being added. Once the reaction vessel had reached thermal equilibrium at 50 °C, the vessel was inserted into the ^{60}Co γ-radiation source until the reaction reached a constant rate. After a steady-state rate had been achieved, the vessel was removed from the γ source and allowed to relax to the new steady-state rate. This procedure was repeated several times; however, only the insertions that were performed when the system was in Interval II were used to determine the exit rate coefficient.

Most chemically-initiated runs were performed with an initiator concentration of 1.0×10^{-4} mol dm^{-3} $K_2S_2O_8$ and a particle number of $N_c \approx 4 \times 10^{16}$ dm^{-3}; these conditions are such that there is no secondary nucleation for either size latex and are convenient for accurate dilatometry.

No relaxation data on the electrostatically-stabilized 44 nm latex could be obtained at pH 4, as coagulation ensued under these conditions. While successful chemically-initiated dilatometry was performed on the electrostatically-stabilized latex at pH 4, the approach to steady state was not observed, since polymerization had commenced before tracking of the meniscus was started, and so no data for ρ and k for the 44 nm electrostatically-stabilized latex are given for pH 4.

Ionic strength was increased by adding NaCl.

Reactions were performed without added buffer. The pH of runs with recipes as in Table 1 was found to be 7 at the start and end of a run. Runs with pH 4 were carried out by adjusting the pH with a 5% solution of HCl, and the pH was found to be virtually unchanged at the end of the polymerization period.

Particle sizes and distributions were obtained using a CHDF-1100 particle size analyzer (Matec Applied Science). Such data were also used to check for the absence of secondary nucleation. The sensitivity of the CHDF was such that particles with a size difference of greater than 20% from the median size are resolved as a secondary population; if two populations close in size are suspected, the sensitivity can be decreased to 10%, as was done for the 24 nm latex. Calibration was through monodisperse standards, with sizes covering the range of the samples.

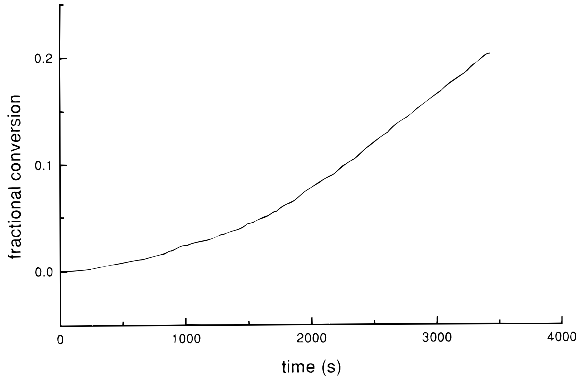

Figure 1. Conversion as a function of time for a typical chemically-initiated run, showing the approach to steady state after the induction period. $N_c = 4.0 \times 10^{16}$ dm^{-3}, [I] = 1.3×10^{-3} mol dm^{-3}, unswollen radius 24 nm, ionically stabilized.

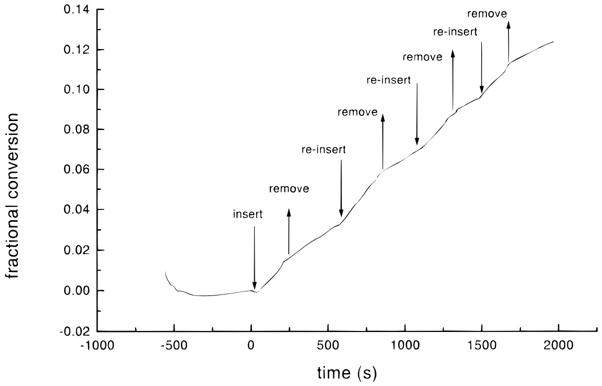

Figure 2. Conversion as a function of time for a typical γ-initiated run, showing approaches to steady state after successive insertions into and removal from the radiation source. $N_c = 4.2 \times 10^{16}$ dm^{-3}, unswollen radius 44 nm, ionically stabilized. Zero conversion set at the commencement of automatic tracking by the dilatometer.

Typical conversion/time data for chemically- and γ-initiated runs are shown in Figures 1 and 2. The means of obtaining exit and entry rate coefficients from such data, using eqs 1 and 2, has been described extensively elsewhere.[3]

4. Results

Results for rate coefficients obtained from all runs are given in Table 3. That portion of these data pertinent to the effect of electrosteric stabilizer are collected in a more easily comprehended format in Figures 3 and 4.

It can be seen from runs 7 and 8 that there is agreement between values of k found by both chemical and γ relaxation, for conditions where an inhibitor/equilibration-artifact-free approach to steady state can be observed with chemical initiator. Exit rate coefficients for a 44 nm electrostatically-stabilized latex, with [I] = 1×10^{-4} mol dm^{-3} for the chemically-initiated run and $N_c = 4.1 \times 10^{16}$ dm^{-3}, were $k = (8 \pm 5) \times 10^{-3}$ s^{-1}; values of $(7.8 \pm 0.5) \times 10^{-3}$ s^{-1} were obtained for the same latex and N_c from γ relaxation. The uncertainties are standard deviations from several runs. This supports the consistency of the means of obtaining rate coefficients from the data.

The first use of these data will be to see if the mechanisms and parameter values leading to eqs 4 and

Table 3. Results from All Runs[a]

run	N_c (10^{16} dm^{-3})	[I] (mol dm^{-3})	$\bar{n}$	ρ(expt.) (s^{-1})	ρ(pred.) (s^{-1})	k(expt.) (s^{-1})	k(pred.) (s^{-1})
24 nm Latex, Ionically Stabilized, pH = 7, No Added Salt							
1	5.8	2.4×10^{-4}	0.18	2.2×10^{-3}			
2	5.8	1.5×10^{-4}	0.20	3.1×10^{-3}	2.8×10^{-3}		
3	5.2	1	0.29	9.0×10^{-3}	8.1×10^{-3}		
4	5.4	γ	0.28	2.5×10^{-4}		$(2.2 \pm 0.5) \times 10^{-2}$	2.1×10^{-2}
25 nm Latex, Electrosterically Stabilized, pH = 7, No Added Salt							
5	4.1	1.3×10^{-4}	0.21	3.1×10^{-4}			
6	4.0	1.3×10^{-4}	0.18	2.0×10^{-4}			
7	4.1	9×10^{-5}	0.22	3.4×10^{-4}		1.0×10^{-3}	
8	5.1	γ	0.35			2×10^{-3}	2.1×10^{-2}
44 nm Latex, Ionically Stabilized, pH = 7, No Added Salt							
9*	1.8	1.2×10^{-3}	0.38	2.6×10^{-2}			
10*	2.3	1.9×10^{-4}	0.28	2.8×10^{-3}			
11*	2.9	6.4×10^{-5}	0.20	1.9×10^{-3}			
12	4.1	1.2×10^{-4}	0.27	2.4×10^{-3}	4.6×10^{-3}		
13	4.2	1.1×10^{-4}	0.26	2.2×10^{-3}	4.3×10^{-3}		
14	4.2	1.2×10^{-4}	0.22	1.4×10^{-3}			
15	5.2	1.0×10^{-3}	0.39	9.2×10^{-3}	8.2×10^{-3}		
16	4.0	γ	0.42	1.4×10^{-3}		$(7.8 \pm 0.5) \times 10^{-3}$	7.3×10^{-3}
49 nm Latex, Electrosterically Stabilized, pH = 7, No Added Salt							
17	1.2	9.5×10^{-5}	0.35	2.6×10^{-4}			
18	1.7	1.4×10^{-4}	0.28	1.2×10^{-4}			
19	2.9	1.2×10^{-4}	0.27	1.4×10^{-4}			
20	2.9	1.2×10^{-4}	0.28	1.1×10^{-4}			
21	1.4	γ	0.15	6.5×10^{-6}		3.3×10^{-4}	7.3×10^{-3}
24 nm Latex, Ionically Stabilized, pH = 4, No Added Salt							
22	5.6	1.6×10^{-4}	0.22	2.7×10^{-3}			
23	3.5	1.1×10^{-4}	0.24	3.4×10^{-3}		2.6×10^{-3}	
24	6.7	γ	0.335	3.2×10^{-4}		$(1.5 \pm 0.5) \times 10^{-2}$	2.1×10^{-3}
25 nm Latex, Electrosterically Stabilized, pH = 4, No Added Salt							
25	4.2	1.2×10^{-4}	0.09	4.7×10^{-4}			
26	3.9	9.3×10^{-5}	0.08	3.1×10^{-4}			
27	3.8	9.8×10^{-5}	0.08	3.5×10^{-4}			
28	6.3	γ	0.31			$(2.4 \pm 0.5) \times 10^{-2}$	2.1×10^{-2}
49 nm Latex, Electrosterically Stabilized, pH = 4, No Added Salt							
31	5.2	1.3×10^{-4}	0.16	6.4×10^{-4}			
32	2.9	9.2×10^{-5}	0.17	6.7×10^{-4}			
33	1.7	γ	0.30	5.3×10^{-4}	$(8 \pm 1) \times 10^{-3}$	7.3×10^{-3}	
24 nm Latex, Ionically Stabilized, pH = 7, Added Salt (6×10^{-3} mol dm^{-3} NaCl)							
34	5.7	1.4×10^{-4}	0.25	1.4×10^{-3}			
35	5.7	1.4×10^{-3}	0.19	3.4×10^{-3}			
36	5.9	γ	0.34	4.4×10^{-4}	$(1.2 \pm 0.4) \times 10^{-2}$	2.3×10^{-2}	
25 nm Latex, Electrosterically Stabilized, pH = 7, Added Salt (6×10^{-3} mol dm^{-3} NaCl)							
37	4.7	1.0×10^{-4}	0.23	1.9×10^{-3}			
38	6.1	9.8×10^{-5}	0.17	8.8×10^{-4}			
39	6.3	γ	0.30	5.5×10^{-4}	$(1 \pm 0.1) \times 10^{-2}$	2.3×10^{-2}	
44 nm Latex, Ionically Stabilized, pH = 7, Added Salt (6×10^{-3} mol dm^{-3} NaCl)							
40	4.0	1.1×10^{-4}	0.25	1.5×10^{-3}	7.2×10^{-3}	7.3×10^{-3}	
41	3.8	1.1×10^{-4}	0.23	9.3×10^{-4}	4.6×10^{-3}	7.3×10^{-3}	
49 nm Latex, Electrosterically Stabilized, pH = 7, Added Salt (6×10^{-3} mol dm^{-3} NaCl)							
42	2.9	1.5×10^{-4}	0.39	1.5×10^{-3}	2.1×10^{-3}	7.3×10^{-3}	
43	2.7	1.1×10^{-4}	0.29	2.7×10^{-3}	6.1×10^{-3}	7.3×10^{-3}	

[a] Uncertainties are from duplicate runs. For chemically-initiated runs where there were inhibitor/equilibration artifacts (indicated by no listed value for k), the value of ρ was obtained from the steady-state value of $\bar{n}$ using eq 3 and the values of k, as listed below, obtained from γ-relaxation runs. For γ runs, the steady-state value of $\bar{n}$ refers to the value in the source, just prior to removal from the source, and the value of ρ is ρ_{thermal} (i.e., after the system has relaxed to its out-of-source steady state). Predicted values of ρ are given by $\rho = \rho_{\text{thermal}} + \rho_{\text{initiator}}$, where the latter is calculated from eqs 9 with the parameter values listed in the text. Experiments marked (with asterisks) commenced in interval III; all other experiments commenced in interval II.

9, which have been extensively tested for other ionically-stabilized styrene systems, can adequately predict the present results. Extensive experimental data for $\rho_{\text{initiator}}$ for a 38 nm unswollen radius styrene latex and persulfate initiator at 50 °C have been fitted[4] with $C_w = 4.3 \times 10^{-3}$ mol dm^{-3},[34] $k_d = 1.3 \times 10^{-6}$ s^{-1},[35] $f' = 0.6$, $z = 3$, $k^1_{p,aq}$ and $k^2_{p,aq} = 1200$ and 300 dm^3 mol^{-1} s^{-1}, and $k_{t,aq} = 8 \times 10^9$ dm^3 mol^{-1} s^{-1}. The values of exit rate coefficients have been fitted[4] with $D_w = 1.5 \times 10^{-5}$ cm^2 s^{-1},[36] $k_{tr,M} = 2.8 \times 10^{-2}$ dm^3 mol^{-1} s^{-1},[37] and $k^1_p = 2.1 \times 10^3$ dm^3 mol^{-1} s^{-1} (8 times the long-chain value, for which there is ample theoretical justification[38]). Using these parameters in eqs 4 and 9 to find ρ and k gave accord that was moderate but not good. It was found that acceptable accord could be obtained by slight variation of these parameters: $k_d = 2 \times 10^{-6}$ s^{-1} (such a change is reasonable because persulfate dissociation can vary because of the presence of small amounts of metal ions, etc.) and $k_{t,aq} = 4 \times 10^9$ dm^3 mol^{-1} s^{-1} (again, this rate coefficient for termination between two charged species in the aqueous phase may well be sensitive to the reaction conditions).

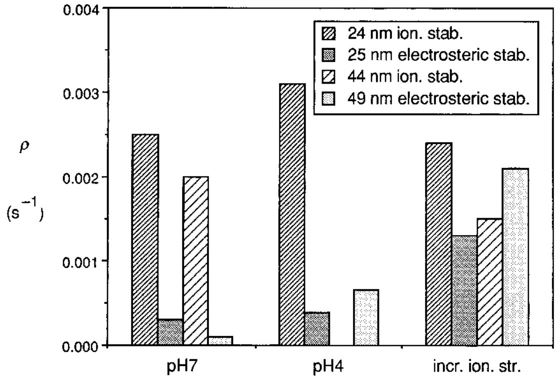

Figure 3. Some entry rate coefficients from Table 3, showing effects of different particle sizes, pH, stabilizer, and ionic strength. For chemically-initiated results, [I] = 1.0×10^{-4} mol dm^{-3} $K_2S_2O_8$; $N_c = 4 \times 10^{16}$ dm^{-3}. No values could be obtained for the ionically-stabilized latex at pH 4 because of coagulation.

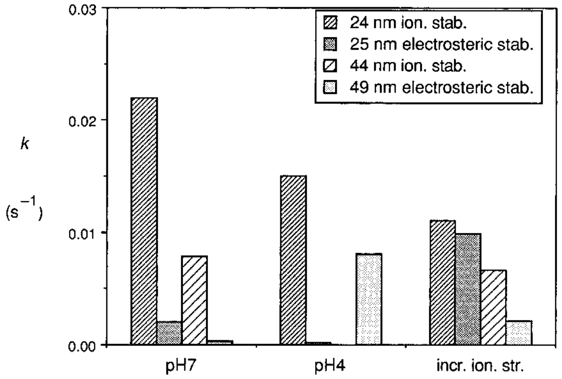

Figure 4. Some exit rate coefficients from Table 3, showing effects of different particle sizes, pH, stabilizer, and ionic strength. For chemically-initiated results, [I] = 1.0×10^{-4} mol dm^{-3} $K_2S_2O_8$; $N_c = 4 \times 10^{16}$ dm^{-3}. No values could be obtained for the ionically-stabilized latex at pH 4 because of coagulation.

The data for an electrostatically-stabilized latex were next used to test the implication of the entry model (discussed above) that ρ should be independent of particle size, provided that all other quantities in the system are the same (the reason that this had not been experimentally tested hitherto was that it is frequently difficult to find identical values of [I] and N_c for two seed latices of very different sizes where secondary nucleation can be avoided while at the same time accurate values of ρ can be obtained). The results for runs 3 and 15 and runs 2 and 14 in Table 3 show clearly that, within experimental uncertainty, the same value of ρ is obtained for 24 and 44 nm latices with the same values of [I] and N_c for electrostatically-stabilized latices. This is regarded as an important verification of one of the major suppositions of the entry model, since it strongly suggests that the entry of a z-mer is not rate-determining (since this entry rate coefficient is highly likely to depend on particle size). This suggests that a powerful test for emulsion polymerization models is that they be able to predict this independence, which should hold for a monodisperse latex under conditions where no particle formation occurs.

Figure 3 shows that there does not seem to be a significant variation of ρ with pH and ionic strength for ionically-stabilized systems, at least over the range of ionic strength and pH where data could be obtained. While this is the first reported study of the effect of pH on entry, the lack of variation with ionic strength is in accord with earlier findings.[21] Figure 4 suggests that there may be some variation of k for electrostatically-stabilized latices with ionic strength and pH, but the variation cannot be said to be outside experimental uncertainty.

The most obvious effect seen in Figures 3 and 4 is that latices stabilized electrosterically have much smaller values of both entry and exit rate coefficients compared to the electrostatically-stabilized latex of essentially the same size, at pH 7. This decrease is much greater than experimental uncertainty in the individual rate coefficients. Moreover, ρ and k for the electrosterically-stabilized latexes show a large variation with particle size, pH, and ionic strength.

The value of ρ with chemical initiator in most cases is much greater than its thermal component ρ_{thermal}, whose value is obtained from the γ-relaxation data as the value of ρ when the system has relaxed to its new steady state out of the radiation source.

The effect of pH on ρ is also large for the electrosterically-stabilized latices: changing the pH from 7 to 4 leads to a significant increase in ρ. The pK_a of acrylic acid is 4.2, and as such the pAA component of the electrosteric stabilizer will be significantly (but not completely) converted to the anion at pH 7, whereas it will be largely in the neutral form at pH 4.

There is some apparent change in ρ with pH for the ionically-stabilized latices, but there are no consistent trends, and the apparent changes are within the experimental uncertainty of ρ (estimated by the scatter in duplicate runs); hence, we are unable to state whether or not there is any effect of change in pH on ρ for ionically-stabilized latices. It is noted that the model for entry given below implies that ρ will be independent of pH.

Changing the pH from 7 to 4 and increasing the ionic strength both result in a large increase in the exit rate coefficient for the electrosterically-stabilized latices. Although there are some apparent changes caused by pH in the exit rate coefficients of electrostatically-stabilized latices in Figure 4, these may or may not be significant compared to the experimental uncertainty, which is typically in the region of 5−10%.

5. Interpretation

The observation that the models of eqs 4 and 9 give acceptable accord with the present data for electrostatically-stabilized latices, using parameters either the same as or only slightly different from those used to fit earlier data for other styrene systems, suggests the correctness of the physical assumptions behind the models for entry and exit. Of particular importance is the confirmation, presented here for the first time, of the prediction that the entry rate coefficient should be independent of particle size, all other quantities being the same. The present data also confirm an earlier observation[21] that the entry rate coefficient is not significantly affected by changes in ionic strength.

The large decrease in both the entry and exit rate coefficients in the electrosterically-stabilized systems can be rationalized if it is assumed that the presence of the electrosteric stabilizer creates a highly viscous region around the particles (a "hairy layer"), which results in a decrease in the rate of diffusion of monomeric (exiting) and oligomeric (entering) species through this region. This would imply that, for entry, eq 8 would become rate-determining, whereas it is not for ionically-stabilized latexes; hence, a z-mer could be terminated while diffusing through this viscous layer before complete entry into the interior of the particle, leading to a decrease in ρ. Similarly, for exit, this viscous region would result in a decrease in D_W in eq 4, leading to a decrease in k (moreover, the slowed exiting radical might be terminated by an entering one, although this, of course, would not occur in the relaxation mode of a γ-initiated system).

These hypotheses are consistent with the observed effect of increasing the ionic strength and changing the pH. Increasing the ionic strength will cause the pAA chains to be compressed on the surface of the particles. The effect of changing pH from 7 to 4 will be to decrease the ionization of the pAA moieties, and hence the chains would tend to collapse upon the particle. Although the viscosity within these collapsed chains will be higher than that in the extended chains, a radical will not have as far to diffuse, and so it is reasonable to suppose that the total time for diffusing through such a layer would be less than that through the extended chains (recall that the accord with experiment for ionically-stabilized latices with eq 4 suggests that diffusion through a thin layer is not rate-determining for such a system). This explains the increase of the entry and exit rate coefficients as the pH goes from 7 to 4, including the observation that the values for pH 4 with electrosteric stabilizer are moderately close to those of the corresponding ionically-stabilized latex, where the latter could be observed (24 nm particles).

Although the changes in ρ and k for the ionically-stabilized latex may be experimental artifacts, such changes, if real, could be ascribed to changes in the nature of a hairy layer surrounding the particles with ionic stabilizer. This is consistent with the variability observed in the exit rate coefficient in latices of essentially the same size but made with minor variations in the preparation procedure.[11]

One way of quantifying the effect of electrosteric stabilizer on entry is to fit the observed value of $\rho_{\text{initiator}}$ to an *effective* degree of polymerization for entry, z_{eff}, through equating the $\rho_{\text{initiator}}$ of eq 9 to the experimental value, using the same values of other parameters as used to fit the data for an electrostatically-stabilized system. This yields values of z_{eff} which are typically 8, rather than 3. The value of $z = 3$ for styrene is physically reasonable, since it is the degree of polymerization at which an $M_iSO_4^-$ entity becomes surface-active.[39] An effective degree of polymerization of 8 is obviously physically unreasonable in terms of the mechanism of eqs 5−8, since such a species would be totally insoluble in water but can be used as a measure of the average degree of polymerization which is achieved by those radicals which avoid termination in the viscous layer long enough to fully enter the interior of the particle.

6. Conclusions

The seeded studies reported in this work show clearly that an electrosteric stabilizer (prepared from a copolymerization of acrylic acid with styrene) has the effect of a major reduction in the rate coefficients for both entry and exit in an emulsion polymerization, compared to what is seen in the same latex with an ionic stabilizer. This reduction varies significantly with changes in both pH and ionic strength and therefore clearly has its origin in the pAA (or polyacrylate) moieties in the interfacial region. The data are consistent with a reduction in the rate at which oligomeric and monomeric radicals diffuse through this hairy layer, due to an increase in the viscosity in this interfacial region.

Hence, in contrast to what is seen in corresponding ionically-stabilized systems, the entry of a surface-active radical species (e.g., $^\bullet(\text{styrene})_2SO_4^-$) into a particle is a rate-determining step in the polymerization with the electrosteric stabilizer used in these studies. That this event is not rate-determining in ionically-stabilized systems was confirmed in the present studies, which showed that the overall rate coefficient for radical entry into particles was independent of the particle size (all other quantities being kept constant).

The variation of the exit rate coefficient with stabilizer is consistent with the transfer-diffusion model for this process, in which diffusion through the aqueous (and hence interfacial) phase away from the particle is usually rate-determining and which therefore would be expected to be affected by local viscosity changes in the interfacial region brought about by the presence of an electrosteric stabilizer.

The effects observed here will have an important influence on particle formation (including secondary nucleation) in systems prepared with ionic comonomers, since entry is a major determining factor in particle formation.[3,4,11]

Acknowledgment. The support of the Australian Research Council and of the Australian Institute for Nuclear Science and Engineering is gratefully acknowledged.

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MA9600567